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Multidimensional Description of the Aromaticity in Planar Five-Membered NSNS Ring Systems

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The effect of the ring-closing fragment on the aromaticity of planar five-membered rings containing an NSNS fragment is investigated systematically. The influence of changing the group or period number of the ring-closing atom is studied as well as the effect of a substituent on this ring-closing element. Two sets of four five-membered ring systems were investigated. To reach a multidimensional description of the aromaticity, a robust set of geometrical, magnetic and energetic aromaticity criteria were combined. π-Electron populations based on the stockholder scheme were calculated and lead to a quantity that correlates to the other aromaticity criteria. A third set of molecules was introduced to verify the conclusions.

1. Introduction

$(SN)_x$-type molecules have received much interest since the discovery of the metallic properties of polymeric $(SN)_x$ in 1973.[1] They are electron-rich materials and such compounds are known to be very reactive. One of the approaches to stabilize these interesting systems, and the one we adopted in our research, is to enclose chains of a limited length, e.g., an $(SN)_2$ unit, in a five- or six-membered ring, thus extending the π-delocalization and stabilizing the heteroatomic fragment. The molecular properties of compounds containing an NSNS fragment, most importantly reactivity and optoelectronic features, differ substantially from those of the corresponding hydrocarbons, which makes these compounds very interesting for investigation. For instance, in previous studies we found both anti-aromaticity ($1,3\lambda^4\delta^2$,2,4-benzodithiadiazine and its derivatives[2,3]) and aromaticity (Roesky's ketone[4] and $CpCoS_2N_2$[5]) in heterocyclic systems containing this NSNS fragment. However, as these compounds differ in more than one parameter, it proved difficult to describe the aromaticity in a systematic way.

The aim of this study is to determine the effect of the ring-closing fragment on the aromaticity of planar five-membered NSNS rings in a more systematic way than was possible with the previous set of compounds mentioned above. Therefore, two series of four molecules were studied that differ from each other in only one parameter. They consist of an NSNS fragment that is closed by boron in 5-bora-1,3,2,4-dithiadiazole, abbreviated [B]-H, by aluminum in 5-alumina-1,3,2,4-dithiadiazole ([Al]-H), by carbon in 1,3,2,4-dithiadiazol-5-yl cation ([C]-H), and by silicon in 5-sila-1,3,2,4-dithiadiazol-5-yl cation ([Si]-H), each with a hydrogen atom exocyclically bound to the ring-closing atom. For the carbon- and silicon-containing compounds the cationic form is used to make them isoelectronic to the other compounds. It is obvious that the first parameters that were studied are the period and group numbers of the ring-closing atom. The third parameter that was varied is the exocyclic substituent bound to the ring-closing atom. To do this, a second series of four molecules was conceived in which the hydrogen atom of the previous series is replaced by chlorine, leading to [B]-Cl, [Al]-Cl, [C]-Cl, and [Si]-Cl, respectively. Again the carbon- and silicon-containing compounds are cations.

Combining the two series of compounds enabled us to relate the changing parameters to the observed trends in the aromaticity. To realize this, a multidimensional description of the aromaticity was set up, combining a number of general aromaticity criteria. These include geometrical (bond length sequences and bond orders), magnetic (NICS values and chemical shifts), and energetic criteria (hardness and HOMO−LUMO gap); in addition, starting from a σ/π-partitioning of the stockholder charges a quantity that correlates to the other criteria was derived.

These particular compounds are difficult to synthesize and manipulate mainly due to their high reactivity. By means of this study we aim to provide a theoretical basis for a more directed search for new compounds in view of their reactivity by describing trends in aromaticity. Furthermore, the selected compounds form a good test set as they all exhibit planarity. This paper is organized in the following way: first, the calculated geometries are discussed and the electron delocalization is studied using geometrical criteria. Thereafter a systematic study of the influence of the ring-closing fragment on the aromaticity is performed on the basis of magnetic, structural and energetic criteria. Then, stockholder π-populations on the NSNS fragment are discussed and trends in aromaticity are predicted for a third set of four molecules with a methyl (CH_3) group as the substituent on the ring-closing atom. Finally, a number of general conclusions are drawn.

To more easily refer to the different compounds or series of compounds throughout the text, a generic formula [X]-Y has been created. In the course of the paper, X can be B, Al, C ,or Si and Y can be H, Cl, or CH_3. E.g., [X]-H designates all compounds with an exocylic hydrogen atom and [Al]-Y designates the three compounds with aluminum as ring-closing atom.

2. Computational Details

All calculations were performed on isolated molecules using the BRABO[6] and Gaussian 98[7] suites of programs applying density functional theory (DFT)[8,9] with the hybrid B3LYP

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TABLE 1: Selected Geometrical Parameters (r_e in Å; Angles in deg) Calculated at the DFT/B3LYP/6-311++G Level of Theory for the Compounds in the [X]-H and [X]-Cl Series**

	[B]-H	[Al]-H	[C]-H	[Si]-H	[B]-Cl	[Al]-Cl	[C]-Cl	[Si]-Cl
S1−N2	1.6692	1.7016	1.6161	1.6538	1.6681	1.7014	1.6145	1.6558
N2−S3	1.6066	1.6006	1.6043	1.6006	1.6064	1.6014	1.6050	1.6016
S3−N4	1.5903	1.5604	1.6472	1.5928	1.5858	1.5611	1.6370	1.5919
N4−X5	1.4102	1.8102	1.2943	1.6650	1.4062	1.8033	1.2977	1.6670
X5−S1	1.8520	2.2510	1.7605	2.1526	1.8610	2.2392	1.7903	2.1557
X5−Y6	1.1816	1.5611	1.0858	1.4653	1.7623	2.0843	1.6844	1.9710

functional[10] and the 6-311++G** basis set.[11,12] Initially, the geometry was calculated in C_1 symmetry but in all cases the structure converted to a planar conformation. Consequently, the symmetry was raised to C_s, the geometry was recalculated, and a frequency calculation was performed to ascertain that the resulting structure was indeed an energy minimum. All calculations of molecular properties were performed at the B3LYP/6-311++G** level using the optimized B3LYP/6-311++G** geometry. Chemical shifts for the hydrogen atoms were obtained by subtracting the chemical shielding values of these atoms from the ones calculated for tetramethylsilane (TMS), being 31.9792 ppm at the B3LYP/6-311++G** level based on the B3LYP/6-311++G** geometry. Nucleus independent chemical shifts (NICS)[13] were calculated in the geometrical center of the ring [NICS(0)] and at a distance of 1 Å perpendicularly above the ring center [NICS(1)].[14] All chemical shift calculations were performed using the gauge independent atomic orbitals (GIAO) method implemented in Gaussian 98. Bond orders were calculated according to Mayer's definition.[15] Stockholder charges were calculated as previously reported,[16] on the basis of the Hirshfeld partitioning of the space.[17] σ/π-Partitioning of the stockholder populations was performed on the basis of the symmetry of the molecular orbitals. The global hardness was calculated from the ionization potential (IP) and electron affinity (EA) according to the well-known formulas.[18] The IPs were calculated by subtracting the energy of the neutral form from that of the cationic form, both calculated at the optimized geometry of the neutral form, only allowing for electronic relaxation for the cation. EAs were calculated in the same way using the energy of the neutral and the anionic form.

3. Results and Discussion

3.1. Geometry. The geometrical results for the eight compounds are presented in Table 1, and the molecular framework and atomic numbering are shown in Figure 1. The NSNS fragment being the most prominent feature of these compounds in view of their (anti/non-)aromaticity, we will start by focusing the discussion mainly on the three NS distances in the molecules. The Lewis structure of the five-membered rings indicates that N2−S3 and S3−N4 have double bond character whereas S1−N2 is a single bond (Figure 1). Taking the NS bond lengths from a previous study on antiaromatic 1,3$\lambda^4\delta^2$,2,4-benzodithiadiazine,[2,3] the values for single and double NS bonds are about 1.717 and 1.566−1.570 Å, respectively, at the B3LYP/6-311+G* level of theory. In all eight molecules of this study, we find a bond length in the very narrow intermediate range between 1.601 and 1.607 Å for the central NS bond, N2−S3, which indicates electron delocalization.[5] The other bond lengths in the NSNS fragment display a larger spread, and this is clearly due to the influence of the fifth ring-closing atom and its substituent.

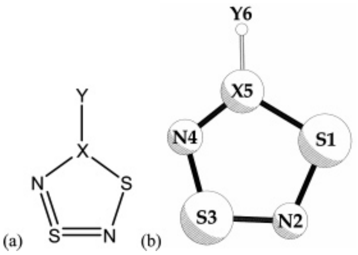

Figure 1. (a) Formal Lewis structure and (b) atomic numbering of the compounds under investigation (X = B, Al, C, Si; Y = H, Cl, CH_3; see text for details).

[B]-H and [C]-H are isoelectronic systems and the same is true for [Al]-H and [Si]-H, but it is important to keep in mind that the total molecular charge is zero for [B]-H and [Al]-H whereas [C]-H and [Si]-H have a net charge of +1. Then, the pertinent differences between the group 13 systems [B]-H and [Al]-H and the group 14 systems [C]-H and [Si]-H are the increased electronegativity and smaller atomic radius for the latter. Table 1 indicates that upon going from [B]-H to [C]-H and from [Al]-H to [Si]-H the longer S1−N2 bond becomes shorter by about 0.05 Å whereas the shorter S3−N4 bond becomes longer by about that same amount. This is a clear indication of delocalization of the electrons within the NSNS fragment upon increasing the atomic number within the same period. In [C]-H it is striking to see that the electrons are delocalized so extensively that the formal double bond S3−N4 becomes longer than the formal single bond S1−N2. The three bonds involving the X atom in [X]-H are systematically larger in [B]-H than in [C]-H and similar trends are found for [Al]-H and [Si]-H, respectively.

We will now investigate the geometrical changes that occur by moving one period down in the periodic table while staying in the same group. The principal quantum number of the valence electrons is now increased by one unit and the ring-closing atom has a larger radius and a smaller electronegativity. When going from [B]-H to [Al]-H and from [C]-H to [Si]-H, we see that in both cases the S1−N2 bond becomes longer and the S3−N4 bond becomes shorter. As a consequence the delocalization is less pronounced in the case of the heavier atoms. As expected and due to the increased atomic radius, the three bonds involving X are systematically larger for Al than for B and the same is true for [C]-H and [Si]-H.

When the same is done for the [X]-Cl series, similar trends are found to those described for the [X]-H systems. The data in Table 1 suggest that substituting the hydrogen atom by chlorine has only a small influence on the geometry of the NSNS fragment. Comparing [B]-H to [B]-Cl and [C]-H to [C]-Cl shows differences in the S3−N4 distance of 0.010 and 0.005 Å, respectively. The differences for the two other NS distances are smaller with values ranging up to a mere 0.002 Å. Equally, comparing [Al]-H to [Al]-Cl and [Si]-H to [Si]-Cl yields a maximum difference of 0.002 Å. This indicates that the heavier ring-closing atoms are more able to neutralize the effect of the change in substituent on the geometry of the NSNS fragment. The largest difference between [X]-H and [X]-Cl for the X−N4 bond is found for aluminum (0.007 Å) and for the X−S1 bond this is 0.030 Å for [C]-Y.

TABLE 2: NICS Values (ppm) in the Plane of the Molecule at the Ring Center [NICS(0)] and at 1 Å above the Ring Center [NICS(1)] of the Compounds in the [X]-H and [X]-Cl Series and ^{1}H NMR Chemical Shifts δ (in ppm vs TMS) of the Hydrogen Atoms in the [X]-H Series

	NICS(0)	NICS(1)	δ
[B]-H	−14.70	−12.35	7.19
[Al]-H	−11.62	−8.91	6.18
[C]-H	−17.90	−14.68	11.49
[Si]-H	−16.57	−12.52	9.19
[B]-Cl	−12.12	−10.23	
[Al]-Cl	−10.97	−8.18	
[C]-Cl	−15.10	−12.28	
[Si]-Cl	−15.22	−11.16	

3.2. Aromaticity. One of the most complicated and debated issues in the field of chemistry, and especially in the domain of computational chemistry, is aromaticity. It is known that aromaticity involves the cyclic electron delocalization coupled with an energetic stabilization but the underlying physical nature of this aromatic stabilization is not known. An extensive set of criteria that can be grouped into structural, energetic, and magnetic criteria can be found in the literature (see for example ref 19), but it is believed that one of them alone cannot lead to the unambiguous definition of aromaticity. In this study we combine a set of criteria to come to a multidimensional description of trends in aromaticity of planar five-membered NSNS ring systems and will introduce an additional quantity based on the charge distribution, which correlates with the other criteria.

3.2.1. Magnetic Criteria. Nucleus independent chemical shift (NICS) values are found to be useful quantities for the description of aromaticity. A negative value indicates aromaticity whereas a positive value indicates antiaromaticity. NICS(0) as well as NICS(1) values were calculated, the latter giving a better quantitative indication for the degree of (anti)aromaticity. Additionally, for the [X]-H series the ^{1}H NMR chemical shifts with TMS as reference were calculated. The chemical shift values of exocyclic hydrogen atoms are known to be a good indication for the aromaticity of organic systems, a higher degree of aromaticity leading to a large chemical shift value. In our case, the results have to be treated more carefully as the difference in electronegativity of the atom to which the hydrogen atom is bound will have an influence on the chemical shift value regardless of the effect of aromaticity. The results of the calculations have been compiled in Table 2.

It can be concluded from the NICS values that all eight molecules are aromatic. Based on the NICS(1) values, the following order of aromaticity [C]-H > [Si]-H > [B]-H > [Al]-H is observed for the [X]-H series. This order is also reflected in the ^{1}H NMR chemical shift values. By moving to the right within the same period, the aromaticity increases, whereas moving downward within the same group leads to a decrease in aromaticity. For the [X]-Cl series the order [C]-Cl > [Si]-Cl > [B]-Cl > [Al]-Cl is suggested by the NICS(1) values, which is in agreement with the results found for the [X]-H series. Furthermore, comparison of both series leads to the conclusion that the hydrogen compounds are more aromatic than their chlorine analogues; however, this trend is less pronounced because the largest difference in NICS(1) values between [X]-H and [X]-Cl is only 2.40 ppm. Thus, replacing the electronically neutral hydrogen atom by an electron-withdrawing chlorine atom causes a slight decrease in the compounds' aromaticity.

TABLE 3: Mayer Bond Orders Calculated for the Compounds in the [X]-H and [X]-Cl Series

	[B]-H	[Al]-H	[C]-H	[Si]-H	[B]-Cl	[Al]-Cl	[C]-Cl	[Si]-Cl
S1−N2	0.99	0.79	1.16	0.94	1.04	0.83	1.14	0.97
N2−S3	1.20	1.23	1.27	1.31	1.21	1.23	1.24	1.30
S3−N4	1.12	1.30	0.95	1.14	1.17	1.23	0.84	1.13
N4−X5	1.31	0.99	1.76	1.27	1.32	1.09	1.67	1.28
X5−S1	1.09	0.97	1.04	1.10	1.05	1.03	0.87	1.00
X5−Y6	1.00	0.94	0.79	0.93	1.27	1.35	1.56	1.38

3.2.2. Structural Criteria. We will now discuss the structural criteria which were already partially covered in the discussion of the geometries (section 3.1). For NSNS-containing compounds it is known that the bond length sequence within the NSNS fragment is a good measure of the electron delocalization and the corresponding aromaticity.[4] We will start here by discussing the results for the [X]-H series. As the middle N2−S3 bond length is the same for the four compounds, we will discuss the degree of aromaticity on the basis of the difference Δ_{NS} between the S1−N2 and the S3−N4 bond lengths. On the basis of Δ_{NS} values of +0.079, +0.141, −0.031, and +0.061 Å for [B]-H, [Al]-H, [C]-H, and [Si]-H, respectively, the four compounds can be placed in the order [C]-H > [Si]-H > [B]-H > [Al]-H in terms of their aromaticity. This order indicates that the aromaticity increases by going to the next element within the same period or by going up within the same group; this is the same as was found on the basis of the magnetic criteria.

Table 3 compiles the calculated bond orders of the two series. It is clear from the table that the bond orders of the S1−N2 and S3−N4 bonds correlate with their respective bond lengths. As a consequence, a further investigation of the difference between these values for each of the molecules leads to the same conclusion as for the bond lengths. When the remaining two values within the ring are investigated, we see that the values of the X5-S1 bond are almost equal for the four compounds and that the differences for the N4-X5 bond are somewhat larger. The latter indicate that there is a strong N4-X5 bond in [C]-H, having a bond order of 1.76, an intermediate bond in [B]-H and [Si]-H, with respective values of 1.31 and 1.27, and a weaker bond in [Al]-H (0.99). A higher bond order value indicates a higher π-contribution to this N4-X5 bond. These values suggest further electron delocalization toward the N4-X5 bond, which is largest in the case of [C]-H and smallest for [Al]-H. As a consequence, these values, together with the bond length sequence within the NSNS fragment, can be used as an indication for the delocalization throughout the whole ring system. This leads to the same order [C]-H > [Si]-H $\approx$ [B]-H > [Al]-H in terms of aromaticity as was found from the bond length sequences.

This discussion based on geometrical parameters can be repeated for the [X]-Cl series, leading to the order [C]-Cl > [Si]-Cl > [B]-Cl > [Al]-Cl, in correspondence with the results for the [X]-H series. Again, these data are in complete agreement with the results based on the magnetic criteria. Comparison between both series is difficult as the differences in bond lengths are relatively small (the differences in bond orders are even smaller). Yet, one could very carefully conclude from the structural data that the chlorine-containing compounds are slightly less aromatic than the hydrogen derivatives, which is in agreement with the magnetic criteria.

3.2.3. Energetic Criteria. Often aromatic compounds are characterized by a large HOMO−LUMO gap. However, the values can only be used in a sensible way when the fragment in which delocalization takes place is the same for the different molecules of which the aromaticity is to be described. Extension of this fragment would lead to a decrease of the HOMO−LUMO gap, which may not have any bearing on a possible effect due to aromaticity. As this condition is satisfied in our study the

TABLE 4: HOMO−LUMO Gap (ϵ, eV) and Global Hardness (η) of the Compounds in the [X]-H and [X]-Cl Series

	ϵ	η
[B]-H	4.603	0.168
[Al]-H	4.169	0.153
[C]-H	5.324	0.188
[Si]-H	4.654	0.167
[B]-Cl	4.254	0.157
[Al]-Cl	4.142	0.152
[C]-Cl	4.369	0.164
[Si]-Cl	4.488	0.161

HOMO−LUMO gaps were calculated for the eight compounds in the [X]-H and [X]-Cl series, and the values are presented in Table 4. The results for the [X]-H series suggest the same order of aromaticity as obtained from the other criteria, i.e., [C]-H > [Si]-H > [B]-H > [Al]-H. When we compare the HOMO−LUMO gaps of the [X]-Cl series to those of the [X]-H series, we see a systematic decrease with the largest difference for the [C]-Y derivatives (0.955 eV). This causes the aromaticity order to be different from that predicted by the other criteria. However, the trends that are found on the basis of the remaining values are in correspondence with the results from the other criteria.

The global hardness is defined as

$$\eta = \frac{\mathrm{IP} - \mathrm{EA}}{2}$$

with IP and EA the ionization potential and electron affinity of the molecule, respectively. In the first approximation and according to Koopmans' theorem, the ionization potential IP of a molecule equals the energy of the HOMO. Analogously, EA can be approximated by the energy of the LUMO. Thus the HOMO−LUMO gap is directly related to the hardness. We chose to calculate a more sophisticated version of these two properties by allowing for electronic relaxation in the calculations of the energies of the radical cation and radical anion, respectively (see section 2). As the hardness is an indication for low reactivity it is larger in the case of more aromatic compounds (see for example ref 18). The calculated values given in Table 4 propose the orders [C]-H > [Si]-H ≈ [B]-H > [Al]-H and [C]-Cl > [Si]-Cl > [B]-Cl > [Al]-Cl for the two series. The differences between the two series are most pronounced for the second-period elements B and C, but all values suggest that the [X]-Cl derivatives are less aromatic. These results are in agreement with the trends that were found from the other criteria.

3.2.4. Electronic Criterion. As aromaticity involves the delocalization of π-electrons throughout a ring system, the last part of this study is used for the calculation of this π-delocalization in terms of electron populations. As was shown, the NSNS fragment takes a prominent place in the electron delocalization and corresponding aromaticity of these compounds. Moreover, this fragment is the only part that is present in all molecules of the two series. Therefore, we calculated the π-stockholder electron population on the NSNS fragment and the values are given in Table 5. The values of the [X]-H series indicate that (the absolute values of) the π-stockholder populations are systematically smaller for the compounds that are more aromatic according to the other criteria. This can be interpreted as a higher degree of delocalization of the π-electrons throughout the entire ring. Exactly the same is found for the compounds in the [X]-Cl series. Smaller absolute values for this new quantity indicate higher aromaticity for the heavier elements within a period and for the lighter elements within a group. These findings are in agreement with the previously discussed criteria.

TABLE 5: π-Electron Population ($|e|$) on the NSNS Fragment for the Compounds in the [X]-H and [X]-Cl Series

	π_{NSNS}
[B]-H	9.392
[Al]-H	9.511
[C]-H	9.089
[Si]-H	9.254
[B]-Cl	9.436
[Al]-Cl	9.530
[C]-Cl	9.185
[Si]-Cl	9.318

TABLE 6: NICS(1) Values (ppm), HOMO−LUMO Gaps (ϵ, eV), Δ_{NS} Values (Å), and π-Electron Populations of the NSNS Fragment ($|e|$) of the Compounds in the [X]-CH_3 Series (Details in Text)

	NICS(1)	ϵ	Δ_{NS}	π_{NSNS}
[B]-CH_3	−11.38	4.452	0.0862	−9.4370
[Al]-CH_3	−8.50	4.150	0.1448	−9.5293
[C]-CH_3	−13.82	5.018	−0.0198	−9.1673
[Si]-CH_3	−11.92	4.582	0.0691	−9.3005

3.3. Evaluation of the Description Using the [X]-CH_3 Series. We will now investigate a third series of molecules and try to predict a number of trends. We would like to emphasize here that all quantities in this study are discussed in the context of trends within a limited set of molecules and not in the context of a quantitative prediction of aromaticity. The third series of molecules is analogous to the two original ones but the compounds now contain a methyl (CH_3) group as the exocyclic substituent; the molecules are abbreviated as [B]-CH_3, [Al]-CH_3, [C]-CH_3 and [Si]-CH_3 for the boron, aluminum, carbon and silicon compounds, respectively. According to the electronegativity of the methyl group, this is expected to generate an inductive effect on the ring intermediate between hydrogen and chlorine. Thus, according to the reduced aromaticity that was found when hydrogen was substituted by chlorine we expect the methyl-substituted molecules to be of intermediate aromaticity. Yet, the small differences that were found between [X]-H and [X]-Cl for a number of quantities have to be kept in mind.

In the case of the [X]-CH_3 compounds, there are two possible C_s conformers, one where the C−H bond in the symmetry plane eclipses the X5-N4 bond and another where it eclipses the X5-S1 bond. Consequently, further geometry optimizations and force field calculations were performed on both conformers of the four molecules in this series. For [B]-CH_3 and [C]-CH_3 the conformation in which the C−H eclipses the X5-S1 bond proved to be an energy minimum, whereas for [Si]-CH_3 the X5-N4 eclipsation yielded the minimum-energy conformer. In each case, the other conformers yielded a higher energy and one imaginary frequency, indicating that these conformers are transition states. For [Al]-CH_3 the two conformers have an equal energy and one small but negative imaginary frequency. We decided to use the conformer in which the C−H eclipses the Al5−S1 bond, with the smallest value of the imaginary frequency.

A number of quantities relating to the different criteria were calculated for the [X]-CH_3 series and have been compiled in Table 6. On the basis of the conclusions drawn for the different aromaticity criteria in the previous sections, we can conclude that the order of aromaticity within this third series is the same as in the other two, i.e., [C]-CH_3 > [Si]-CH_3 > [B]-CH_3 > [Al]-CH_3. For the magnetic and energetic criteria, represented by the NICS(1) value and the HOMO−LUMO band gap, it is clear that the aromaticity of the [X]-CH_3 series is indeed intermediate, as expected. In addition, the values of the π-stockholder population density on the NSNS fragment are completely compatible with the other criteria and reproduce the expected intermediate aromaticity. Finally, the structural criterion, the difference Δ_{NS} between the S1−N2 and the S3−N4 bond lengths, confirms the correct order within the third series of molecules.

4. Conclusions

By combining magnetic (^{1}H NMR shifts and NICS values), structural (bond length differences and bond orders), and energetic (HOMO−LUMO gap and hardness) criteria, we were able to provide a multidimensional description of the trends in aromaticity for a series of planar isoelectronic five-membered rings containing an NSNS fragment. Regarding the influence of the ring-closing atom on the aromaticity, the following conclusions can be drawn. (i) Shifting to the next group within the same period increases the aromaticity. (ii) Shifting to the next period within the same group causes a decrease in aromaticity. (iii) Increasing the electronegativity of the substituent bound to the ring-closing atom slightly decreases the aromaticity. The π-electron population on the NSNS-fragment was found to be a good indication for the degree of aromaticity in these isoelectronic systems, predicting the same trends as the other aromaticity criteria.

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